

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2003-171544**

(43)Date of publication of application : **20.06.2003**

(51)Int.Cl.

C08L 67/04

C08J 5/00

C08K 5/14

(21)Application number : **2002-088378**

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(22)Date of filing : **27.03.2002**

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(30)Priority

Priority number : **2001302048** Priority date : **28.09.2001** Priority country : **JP**

(54) LACTIC ACID RESIN COMPOSITION, PEROXIDE-MODIFIED LACTIC ACID RESIN COMPOSITION, AND THEIR MOLDED ITEMS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lactic acid resin composition and a peroxide-modified lactic acid resin composition, both excellent in processability and physical properties in addition to biodegradability inherent in a lactic acid resin; and molded items obtained from them.

SOLUTION: The lactic acid resin composition comprises 100 pts.mass lactic acid resin and 0.05-5.0 pts.mass organic peroxide having a 1-hr half-life temperature (Th1) of 70-200°C and, preferably, a hydrogen abstraction coefficient (ϵ) of 10-60. The peroxide-modified lactic acid resin composition is prepared by subjecting the lactic acid resin composition to a reaction by a specific means so as to satisfy the relation represented by the equation: $D2/D1=1.10-3.0$ (wherein D1 is the polydispersity of the composition before the reaction; and D2 is that after the reaction). Molded items are prepared from these compositions.

LEGAL STATUS

[Date of request for examination]

01.02.2005

[Date of sending the examiner's decision of rejection]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the lactic-acid system resin constituent excellent in the moldability, a peroxide denaturation lactic-acid system resin constituent, and the Plastic solid that made them the raw material and carried out the fabricating operation.

[0002]

[Description of the Prior Art] Decomposing and disappearing with time and not having an adverse effect on natural environment eventually from a rise of an environmental problem, in recent years, when a plastic is rejected in natural environment is beginning to be called for. Conventional plastics was stable over the long period of time in natural environment, and moreover, since relative bulk density was small, the trouble of having promoted the ephemeralization of a trash reclaimed ground or spoiling a natural scene and the living environment of wildness animals and plants was pointed out.

[0003] Then, biodegradability plastic material attracts attention today. Biodegradable plastics are the inside of soil, and underwater, breaking and decomposition advance gradually according to hydrolysis or biodegradation, and becoming a harmless decomposition product according to an operation of a microorganism eventually is known. As a biodegradable plastic which is beginning to be put in practical use, polylactic acid, aliphatic series polyester, Denaturation PVA, a cellulose ester compound, starch modification objects, these blend objects, etc. exist. Although biodegradability plastic material has the description of a proper, respectively and application expansion according to these is achieved, lactic-acid system resin is resin of a few hard systems in this, and the alternative of hard system resin, such as polyethylene terephthalate (PET), and polystyrene (PS), ABS, is expected.

[0004] However, lactic-acid system resin had the fault that melting tension is relatively low, and strain-hardening nature was also scarce and inferior to workability. since melting tension and strain-hardening nature are relatively low -- for example, tubular blown film shaping -- setting -- that a bubble is not stabilized **** -- sheet forming -- setting -- that the drawdown of a sheet occurs at the time of preheating **** -- blow molding -- setting -- that parison deforms **** -- foaming -- setting -- that foam breaking occurs mostly **** -- etc. -- there was a trouble.

[0005] Although the method of improving copolymerizing the polyfunctional monomer of the branching nature which raises molecular weight etc. can be considered in order to raise melting tension, melt viscosity goes up beyond the need, productivity, such as extrusion discharge quantity, falls, and, on the other hand, the industrial acquisition of lifting of molecular weight is not easy for the polyfunctional monomer of branching nature.

[0006] Although JP,11-286570,A had disclosure of a constituent at JP,01-26658,A about the attempt which raises melting tension by addition of a peroxide in the blend of lactic-acid system resin and other aliphatic series polyester resin in foaming, these specified neither the class of peroxide, nor the form of a reaction denaturation object, and were not necessarily what has effectiveness in moldability amelioration.

[0007]

[Problem(s) to be Solved by the Invention] That is, the technical problem of this invention offers the lactic-acid system resin constituent which has the workability in which lactic-acid system resin was excellent in addition to the biodegradability which it originally has, and physical properties, a peroxide denaturation lactic-acid system resin constituent, and the Plastic solid with which it consists of them.

[0008]

[Means for Solving the Problem] this invention persons came to complete high this invention of effectiveness, as a result of repeating examination wholeheartedly in view of such the actual condition. Invention concerning this application is invention indicated to the following (1) - (5).

(1) The lactic-acid system resin constituent which serves as the lactic-acid system resin 100 mass section from the organic peroxide 0.05 whose half-life temperature $T_{1/2}$ is 70-200 degrees C - the 5.0 mass sections for 1 hour.

(2) The lactic-acid system resin constituent which serves as the lactic-acid system resin 100 mass section from the organic peroxide 0.05 70-200 degrees C and whose hydrogen drawing multiplier epsilon the half-life temperature $T_{1/2}$ is 10-60 - the 5.0 mass sections for 1 hour.

(3) Peroxide denaturation lactic-acid system resin which is $D_2/D_1=1.10-3.0$ when the above-mentioned lactic-acid system constituent is made to react with a predetermined means, polydispersed degree of the lactic-acid system resin before a peroxide reaction is set to D_1 and polydispersed degree of the lactic-acid system resin after a peroxide reaction is set to D_2 . In this invention, a predetermined means means means, such as heating and radiation irradiation.

(4) The Plastic solid of the film which consists of the above-mentioned peroxide denaturation lactic-acid system resin, a sheet, a sheet Plastic solid, a foaming sheet, a foaming sheet Plastic solid, a blow molding object, an injection-molding object, mold foam, fiber, a pipe, a plate, a plate Plastic solid, etc.

(5) The constituent which consists of lactic-acid system resin 50 - the 97 mass sections, and the organic peroxide 0.05 70-200 degrees C and whose hydrogen drawing multiplier epsilon aliphatic series polyester 0 degree C or less or/and aliphatic series aromatic polyester 3 - 50 mass sections, and the 1-hour half-life temperature $T_{1/2}$ are 10-60 for glass transition temperature T_g - the 5.0 mass sections.

(6) The Plastic solid of the film which carried out the fabricating operation after making the above-mentioned lactic-acid system resin constituent react with predetermined means, such as heating and radiation irradiation, a sheet, a sheet Plastic solid, a foaming sheet, a foaming sheet Plastic solid, a blow molding object, an injection-molding object, mold foam, fiber, a pipe, a plate, a plate Plastic solid, etc.

[0009]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The lactic-acid system resin in this invention may mean Pori (DL-lactic acid) Pori (L-lactic acid) whose structural unit is L-lactic acid, Pori (D-lactic acid) whose structural unit is D-lactic acid, and whose structural units are L-lactic acid and D-lactic acid, and these mixtures, and may be a copolymer with alpha-hydroxycarboxylic acid, or diol/dicarboxylic acid further.

[0010] As a polymerization method of lactic-acid system resin, any well-known approaches, such as a condensation polymerization method and a ring-opening-polymerization method, are employable. for example, a condensation polymerization method -- if -- the lactic-acid system resin which carried out direct dehydration condensation polymerization of L-lactic acid, D-lactic acids, or such mixture, and had the presentation of arbitration can be obtained.

[0011] Moreover, by the ring-opening-polymerization method, a polylactic acid system polymer can be obtained using the catalyst chosen in the lactide which is the annular dimer of a lactic acid while using the modifier etc. if needed. There are L-lactide which is the dimer of L-lactic acid, D-lactide which is the dimer of D-lactic acid, and a DL-lactide which consists of L-lactic acid and a D-lactic acid further as lactide, and lactic-acid system resin with the presentation of arbitration and crystallinity can be obtained by mixing and carrying out the polymerization of these if needed.

[0012] Furthermore, non-aliphatic series diol like non-aliphatic series dicarboxylic acid like a terephthalic acid and/or the ethyleneoxide addition product of bisphenol A as a little copolymerization component may be used if needed for raising thermal resistance etc. A small amount of chain elongation agent, for example, a diisocyanate compound, an epoxy compound, an acid anhydride, etc. can be used

for the purpose of molecular-weight buildup further again.

[0013] As other above-mentioned hydroxycarboxylic acid units by which copolymerization is carried out to lactic-acid system resin The optical isomer of a lactic acid (to L-lactic acid, it is L-lactic acid to D-lactic acid and D-lactic acid), A glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, 2-hydroxy-n-butanoic acid, 2-hydroxy - Lactone, such as 2 organic-functions aliphatic series hydroxycarboxylic acid and caprolactones, such as 3 and 3-dimethyl butanoic acid, 2-hydroxy-3-methyl butanoic acid, 2-methyl lactic acid, and a 2-hydroxy caproic acid, a butyrolactone, and a valerolactone, is mentioned.

[0014] As the above-mentioned aliphatic series diol by which copolymerization is carried out to lactic-acid system resin, ethylene glycol, 1,4-butanediol, 1, and 4-cyclohexane dimethanol etc. is raised.

Moreover, as the above-mentioned aliphatic series dicarboxylic acid, a succinic acid, an adipic acid, a suberic acid, a sebacic acid, dodecane diacid, etc. are mentioned.

[0015] As range where the weight average molecular weight of lactic-acid system resin is desirable, it is 50,000-400,000 and is 100,000-250,000 preferably. When the weight average molecular weight of lactic-acid system resin is less from 50,000, practical use physical properties are hard to be discovered, and when exceeding from 250,000, melt viscosity is too high and may be inferior to fabricating-operation nature.

[0016] the 1st voice of this invention -- the lactic-acid system resin constituent applied like is a resin constituent which added the organic peroxide 0.05 whose half-life temperature (Th1) is 70-200 degrees C - the 5.0 mass sections to the lactic-acid system resin 100 mass section for 1 hour.

[0017] the 2nd voice of this invention -- the lactic-acid system resin constituent applied like is a resin constituent with which half-life temperature (Th1) added the organic peroxide 0.05 70-200 degrees C and whose hydrogen drawing multiplier (epsilon) are 10-60 - the 5.0 mass sections to the lactic-acid system resin 100 mass section for 1 hour.

[0018] It is the derivative of a hydrogen peroxide (H-O-O-H), and organic peroxide has the structure which permuted one hydrogen atom of a hydrogen peroxide, or two pieces with the organic free radical, and is a compound characterized by having one or more peroxide association (O-O) in the intramolecular.

[0019] As a class of peroxide, a ketone peroxide system, a diacyl peroxide system, a hydroperoxide system, the dialkyl peroxide system, the peroxy ketal system, the alkyl par ester system, the par carbonate system, etc. are known widely.

[0020] However, in order to improve the moldability of lactic-acid system resin, it is necessary to choose a compound with the specific engine performance among these. That is, it is indispensable that half-life temperature (Th1) chooses preferably 70-200 degrees C of organic peroxide which is 100-160 degrees C for 1 hour. Furthermore, it is desirable 10-70, and that a hydrogen drawing multiplier (epsilon) chooses preferably 10-60, and the organic peroxide that is 20-60 still more preferably.

[0021] Here, 1-hour half-life temperature (Th1) is temperature which a peroxide decomposes and the one half of an initial mass decomposes with heat in 1 hour. If half-life temperature (Th1) is less than 70 degrees C for 1 hour, a peroxide decomposes also at a room temperature and is not desirable on insurance and a life cycle. Moreover, when making it react with lactic-acid system resin, exothermic reaction is too sudden, and it is not desirable to deactivate, before reacting locally, generating gel in resin or reacting [**** / pyrolyzing resin] to reverse with resin etc. In exceeding from 200 degrees C, it is hard coming to progress on conditions with a common reaction of degeneration. What fulfills these conditions out of a commercial item for 1 hour as organic peroxide whose half-life temperature (Th1) is 70-200 degrees C may be chosen suitably. For example, the trade name "PERKADOX BC" (1= 132 degrees C of Th) by Kayaku AKZO Corp. can come to hand commercially.

[0022] Fabricating-operation nature can be raised by kneading the organic peroxide whose half-life temperature (Th1) is 70-200 degrees C to lactic-acid system resin for 1 hour. A bridge formation-reaction occurs by kneading predetermined organic peroxide to lactic-acid system resin, and it thinks for the viscosity of a linearity field to rise as the result.

[0023] When a hydrogen drawing multiplier (epsilon) heats organic peroxide at half-life temperature with the concentration of the inside of n-pentadecane, and 0.2 mol/L in this invention for 30 minutes for

15 minutes and it is made to decompose, it is the relative comparison numeric value of the amount of n-pentadecane dimer to generate. However, the amount when using 2 and 2'-azobis (isobutyronitrile) was set to 1. If a hydrogen drawing multiplier (epsilon) is less from 10, the moldability amelioration effectiveness of lactic-acid system resin will be hard to be acquired. Moreover, composition is difficult for the organic peroxide which it exceeds from 70, and it is not easy to receive including a cost side.

[0024] As organic peroxide 70-200 degrees C and whose hydrogen drawing multiplier (epsilon) half-life temperature (Th1) is 10-70, the following compounds can illustrate typically for 1 hour.

1 and 1-G t-butylperoxycyclohexane (1= 113 degrees C of Th) epsilon= 24 degrees C, t-butylperoxy-3,5,5-trimethyl hexanoate (1= 114 degrees C of Th) epsilon= 33, 2,2-Di-t-butyl-peroxy-butane (1= 116 degrees C of Th) epsilon= 24, t-butylperoxyisopropylcarbonate (1= 117 degrees C of Th) epsilon= 40, tert-butyl peroxide-2-ethylhexyl carbonate (1= 117 degrees C of Th) epsilon= 40, t-amyl peroxy benzoate (1= 118 degrees C of Th) epsilon= 39, t-butyl peroxyacetate (1= 119 degrees C of Th) epsilon= -- 43, 4, and 4-G tert-butyl peroxide valeric-acid-n-butylester (1= 121 degrees C of Th) epsilon= 24, t-butyl peroxybenzoate (1= 122 degrees C of Th) epsilon= -- 49, 2, the 5-dimethyl -2, and 5-G (tert-butyl peroxide) hexane (1= 134 degrees C of Th) epsilon= -- 41, 1, and 3-screw-(t-butyl PAOKI seesaw propyl) benzene (1= 134 degrees C of Th) epsilon= 55, t-butyl cumyl peroxide (1= 136 degrees C of Th, epsilon= 41), di-t-butyl peroxide (1= 141 degrees C of Th, epsilon= 49), 2, the 5-dimethyl -2, 5-G (tert-butyl peroxide) hexyne -3 (degrees C [of Th / 1= 141], epsilon= 30)

70-200 degrees C and a hydrogen drawing multiplier (epsilon) may choose suitably that with which half-life temperature (Th1) fills these conditions out of a commercial item for 1 hour as organic peroxide which is 10-70. For example, the trade name "Trigonox 22" by Kayaku AKZO Corp., "Trigonox 42", "Trigonox D", etc. can come to hand commercially.

[0025] here -- the lactic-acid system resin 100 mass section -- receiving -- organic peroxide 0.05 - the 5.0 mass sections -- the 0.1 - 3.0 mass section is added preferably. If the addition of an organic-ized oxide is smaller than the 0.05 mass section, the moldability of lactic-acid system resin is hard to be improved, and when larger than 5.0, the whole resin will construct a bridge, plasticity will become scarce, and it will lose workability conversely.

[0026] Although it is an extruder and a batch type kneader, and the approach of carrying out melting kneading is common as an approach to which the above-mentioned lactic-acid system resin constituent is made to react, heating at 130-240 degrees C, it fixes to a mold, and it can reheat with an air-heating furnace, or can also be made to react by radiation irradiation, after [80-130 degrees C] low-temperature-melting-kneaded or solution kneading. After fabricating to a medium Plastic solid, a peroxide and lactic-acid system resin may be made to react in this approach. A medium Plastic solid points out a thing like the extrusion sheet in the case of obtaining the vacuum-forming article and press-forming article from a sheet.

[0027] Next, although the above-mentioned constituent is made to react with means, such as heating and radiation irradiation, in this invention, if polydispersed degree of the lactic-acid system resin before a peroxide reaction is set to D1 and polydispersed degree of the lactic-acid system resin after a peroxide reaction is set to D2 at this time, it is important preferably $D2/D1=1.10-3.0$ and to control in the range of 1.3-2.2.

[0028] If the above $D2/D1$ is less than this range, when the moldability of lactic-acid system resin will be improved, it will be hard and it will exceed, a large and small gel object is generated, an appearance may be spoiled or lowering of machine physical properties may be brought about. Furthermore, even if it increases, strain-hardening nature may fall, or the bleeding of oligomer may generate melting tension.

[0029] Since the thing 70-200 degrees C and whose hydrogen drawing multiplier (epsilon) half-life temperature (Th1) be 10-60 and to do for an organic peroxide 0.05-5.0 mass section activity be strongly influence for 1 hour of the property of existence of heating time, a shear rate, content moisture regain, and a specific metal and the reaction residue of a peroxide etc. in addition to it although it be the most important in order to control $D2/D1$ in this range, it be adjust suitably, look at D2.

[0030] For example, when the residue of long duration heating in an extruder, existence of moisture, and a peroxide becomes the acid, $D2/D1$ tends to become large. Moreover, it is in the inclination which

becomes small in high shearing, short-time heating, and radiation irradiation.

[0031] As mentioned above, melting tension rises, strain-hardening nature is discovered, and the lactic-acid system resin resin constituent (peroxide conversion lactic-acid system resin constituent) which denaturalized with the peroxide comes to have a good moldability. Therefore, a peroxide lactic-acid system resin constituent is used suitable for the film which needs melting tension at the time of shaping, a sheet, a sheet Plastic solid, a foaming sheet, a foaming sheet Plastic solid, a blow molding object, an injection-molding object, mold foam, fiber, a pipe, a plate, a plate Plastic solid, etc.

[0032] For example, the following effectiveness is expected.

- 1) A bubble is stabilized in a tubular blown film.
- 2) Prevent the feeding neck at the time of the extrusion cast with a sheet.
- 3) In a sheet Plastic solid, prevent the drawdown at the time of preheating and raise thickness distribution of a Plastic solid.
- 4) With a foaming sheet, make the cellular structure uniformly and precise and prevent foam breaking.
- 5) In a foaming sheet Plastic solid, prevent the drawdown at the time of preheating and raise thickness distribution of a Plastic solid.
- 6) With a blow molding object, prevent the drawdown of parison and raise thickness distribution of a Plastic solid.
- 7) Prevent weld flash with an injection-molding object.
- 8) In mold foam, make the cellular structure uniformly and precise and prevent foam breaking.
- 9) For fiber, raise the stringiness at the time of spinning and prevent the thread breakage.
- 10) Raise the configuration stability at the time of extrusion in a pipe.
- 11) Prevent the drawdown at the time of level extrusion on a plate.
- 12) In a plate Plastic solid, prevent the drawdown at the time of preheating and raise thickness distribution of a Plastic solid.

[0033] In this invention, glass transition temperature T_g can also blend aliphatic series polyester resin and aliphatic series aromatic polyester resin 0 degree C or less to a lactic-acid system resin constituent.

[0034] As the above-mentioned aliphatic series polyester resin, the aliphatic series polyester obtained by condensing aliphatic series diol and aliphatic series dicarboxylic acid, the aliphatic series polyester which carried out ring opening polymerization of the annular lactone, synthetic system aliphatic series polyester, etc. are mentioned, for example.

[0035] Out of ethylene glycol [which is aliphatic series diol], 1,4-butanediol and 1, and 4-cyclohexane dimethanol, etc. the succinic acid which is aliphatic series dicarboxylic acid, an adipic acid, a suberic acid, a sebacic acid, dodecane diacid, etc., one or more kinds of aliphatic series polyester obtained by condensing the above-mentioned **** diol and aliphatic series dicarboxylic acid is chosen, carries out a condensation polymerization, and is obtained, respectively. It can jump up with an isocyanate compound etc. if needed, and a desired polymer can be obtained. As a commercial raw material pellet, Bionolle by Showa High Polymer Co., Ltd. etc. is illustrated.

[0036] Moreover, in order to raise thermal resistance and mechanical strength, aromatic series monomer components, such as a terephthalic acid not more than 50mol%, can also be copolymerized as a dicarboxylic acid component. The resin by which copolymerization was carried out in such a form corresponds to the aliphatic series aromatic polyester as used in the field of this invention. As a commercial raw material pellet, the Easter biotechnology by the Eastman chemical company, Eko FREX by BASF A.G., etc. are illustrated.

[0037] As aliphatic series polyester which carried out ring opening polymerization of the above-mentioned annular lactone, it is mentioned typically, and epsilon-caprolactone which is an annular monomer, delta-valerolactone, one or more kinds of beta-methyl-delta-valerolactones, etc. are chosen from these, and a polymerization is carried out.

[0038] As the above-mentioned synthetic system aliphatic series polyester, a copolymer with a cyclic anhydride, oxiranes, for example, a succinic anhydride and ethyleneoxide, propylene oxide, etc. is mentioned.

[0039] When blending aliphatic series polyester resin etc. to a lactic-acid system resin constituent, not

only the workability of lactic-acid system resin but shock resistance and cold resistance can be improved by considering as the lactic-acid system resin constituent with which glass transition temperature (Tg) serves as lactic-acid system resin from aliphatic series polyester 0 degree C or less and/or aliphatic series aromatic polyester, and organic peroxide. Moreover, [0040] by which mechanical strength and transparency are improved by adding organic peroxide compared with a simple blend system with lactic-acid system resin, aliphatic series polyester, and/or aliphatic series aromatic polyester As a compounding ratio (the mass section shows) of each component, lactic-acid system resin:(aliphatic series polyester and/or aromatic series aliphatic series polyester):organic peroxide =50-97:3-50:0.05-5.0 (mass section) is desirable. When the shock resistance and the cold-resistant amelioration effectiveness which will be considered as a request if [than the range which requires the loadings of lactic-acid system resin] more are scarce and there are, it is inferior to rigidity or abrasion-proof nature. [little] [0041] Moreover, additives, such as a thermostabilizer, an anti-oxidant, UV absorbent, light stabilizer, a pigment, a coloring agent, lubricant, a nucleating additive, a hydrolysis inhibitor, and an inorganic filler, can also be prescribed in the range which does not spoil the effectiveness of this invention. [0042] Beforehand, using this direction biaxial extruder, a kneader, a Henschel mixer, etc. as an approach of obtaining a constituent, a pre compound may be carried out, the dryblend of each raw material may be carried out, and it may be fed into a direct making machine. A making machine is not limited especially in order to attain this invention.

[0043]

[Example] Although an example is shown below, this invention does not receive a limit at all by these. In addition, on conditions as shown below, the measured value shown in an example measured and was computed.

[0044] 1) 1-hour half-life temperature of organic peroxide (Th)

Organic peroxide and the solution of 0.2 mol/L are prepared using benzene as a solvent. It extracts 15 mLs of four sample solutions at a time in compressive test tubing. It seals by nitrogen's permuting four proof-pressure containers beforehand, and putting the test tube to which the sample solution was paid into each proof-pressure container. A proof-pressure container is simultaneously put in during the glycerol bath set as the measurement temperature assumed from the measurement result in DSC. One proof-pressure container is taken out out of a glycerol bath after 15 minutes, and it is promptly immersed into iced water and cools. From the proof-pressure container after cooling, the amount of active oxygen (A. O%) is measured for a test tube by ejection and the iodometry method, and this is made into 0 hour. After that, the amount of active oxygen (A. O%) is measured in the same way to every fixed time amount (2 hours, 4 hours, 6 hours), and it is asked for the half line in each temperature. Temperature is plotted on an axis of abscissa, half line is plotted on an axis of ordinate, and the half-life temperature Th is searched for from the graph for 1 hour. Moreover, in order to ask for the hydrogen drawing multiplier shown below, half-life temperature was also read in this graph for 15 minutes.

[0045] 2) The hydrogen drawing multiplier of organic peroxide (epsilon)

Organic peroxide was dissolved in n-pentadecane by 0.2 mol/L concentration, and it considered as the sample solution. This sample solution was extracted in 20mL test tubes, and it was immersed in the glycerol, and heated at half-life temperature for 30 minutes for 15 minutes. The amount of n-pentadecane dimer generated at this time was measured, and relative evaluation was carried out, having used as 1 the amount of n-pentadecane dimers generated when 2 and 2'-azobis (isobutyronitrile) is used.

[0046] 3) D -- 2 / gel-permeation-chromatography HLC[by D1 TOSOH CORP.]-8120GPC was equipped with GPC-800CP of the chromatographic column Shim-Pack series by Shimadzu Corp., and it measured at a part for solvent chloroform, solution concentration 0.2 wt/vol%, and solution injection rate 200microL and solvent rate-of-flow 1.0mL/, and the solvent temperature of 40 degrees C. By polystyrene conversion, weight average molecular weight was computed in the number average molecular weight of the lactic-acid system resin before and behind a reaction, and a list. The weight average molecular weight of the used standard polystyrene is 2 million, 670000, 110000, 35000, 10000, 4000, and 600. The value which ** (ed) weight average molecular weight with number average molecular weight is polydispersed degree. Many powder after D1 and a reaction was set to D2 for the

polydispersed degree before an organic peroxide reaction, and D2/D1 was computed.

[0047] 4) It is Kurimoto Factory SK about a strain-hardening nature lactic-acid system resin constituent. KRC kneader Using N 90-1, it kneaded by 190 degrees C and 200rpm, and at 190 degrees C, the kneading object was pressed for 10 minutes, and was annealed with 100t press. The press plate was cut down to width-of-face x die-length x thickness = 7x55x1.5mm, and was made into the sample for 1 shaft extension measurement of viscosity. 1 shaft extension viscosity was measured for this sample by rate of strain regularity (0.5sec-1) at 190 degrees C under nitrogen-gas-atmosphere mind using RME by REOMETO Rix Corp. From the graph, whenever [strain-hardening] was computed by the following formulas.

strain-hardening whenever = $(\eta_5 - \eta_1) / \eta_1$ -- here -- the extension viscosity 5 seconds after [of a 1 second after / the η_1 = measuring time] the extension viscosity η_5 = measuring time [0048] 5) 30mm [by Mitsubishi Heavy Industries, LTD.] phi single screw extruder (l/d=22) equipped with the kneading zone was presented with the rate lactic-acid system resin constituent of the neck in of an extrusion sheet, and sheet extrusion with a thickness of 100 micrometers was performed from the width-of-face [of 200mm], and lip gap 1mm mouthpiece by the laying temperature of 190 degrees C, rotational frequency 30rpm, and discharge quantity 3 kg/h. the mouthpiece when adjusting a taking over rate and setting thickness of a sheet to 100 micrometers (taking over rate = about 4m) -- sheet width of face just behind an outlet was set to L1, sheet width of face of the place distant from the mouthpiece 20cm was set to L2, and the rate of the neck in was computed by the following formula. As for the rate of the neck in, in general sheet forming, it is desirable that it is 10% or less.

Rate of the neck in (%) = $(L1 - L2) / L1 \times 100$ [0049] 6) 30mm [by Mitsubishi Heavy Industries, LTD.] phi single screw extruder (l/d=22) equipped with the kneading zone was presented with what added the foaming agent ACDA(AZOJI carvone amide) 1 mass section, and sheet extrusion with a thickness of 500 micrometers was performed to the diameter lactic-acid system resin constituent of a cel of a foaming sheet from the width-of-face [of 200mm], and lip gap 1mm mouthpiece by the laying temperature of 190 degrees C, rotational frequency 30rpm, and discharge quantity 3 kg/h. The cutter cut the extruded sheet to the flow direction, and observation by the optical microscope was performed. The particle diameter of a foaming cel was measured visually and it computed on the average about ten foaming cels in a visual field. Moreover, the overall condition of a foaming cel was also observed. In the usual foaming extrusion sheet forming, the diameter of a cel is 100 micrometers or less; it is uniform and it is desirable that there is no foam breaking.

[0050] 7) The sample was started in width-of-face [of 10mm] x die-length [of 80mm] x thickness of 4mm, and it examined by the notch and edge WAIZU (notch type A) to the longitudinal direction of a Charpy impact strength pipe using the Yasuda energy machine factory Charpy impact tester based on JIS-K7111. A unit is KJ/m2.

[0051] (Example 1) As lactic-acid system resin, Lacty 5000 (weight average molecular weight 200,000, polydispersed degree 2.0) by Shimadzu Corp. which is a gay's polylactic acid was used. In this lactic-acid system resin 100 mass section, the 0.4 sections (the Nippon Kayaku Co., Ltd. make, trade name "RAUROKKUSU") (1= 79 degrees C of Th, epsilon= 8) of lauroyl peroxide are added as organic peroxide, and it is Kurimoto Factory SK. KRC kneader Using N 90-1, it kneaded by 190 degrees C and 200rpm, and the strand was extruded, in the cistern, after quenching, the strand cut was carried out and the pellet was obtained. When it asked for the rate of the neck in, and the diameter of a foaming cel whenever [strain-hardening] using the obtained pellet, the diameter of a foaming cel of 4.8 and the rate of the neck in was 120 micrometers (homogeneity) 12% whenever [strain-hardening].

[0052] (Examples 2-4, examples 1-3 of a comparison) As lactic-acid system resin, Lacty 5000 (weight average molecular weight 200,000, polydispersed degree 2.0) by Shimadzu Corp. which is a gay's polylactic acid was used. To this lactic-acid system resin, the organic peroxide shown in a table 1 is added, and it is Kurimoto Factory SK. Using the KRC kneader N 90-1, it kneaded by 190 degrees C and 200rpm, and the strand was extruded, in the cistern, after quenching, the strand cut was carried out and the pellet was obtained. The above-mentioned assessment was performed using the obtained pellet. These assessment results are shown in a table 1.

[0053]

[A table 1]

	比較例 1	実施例 2	実施例 3	実施例 4	比較例 2	比較例 3
有機過酸化物	なし	t-ブチルパー オキシベンゾエ ート	t-ブチルパー オキシベンゾエ ート	2,5-ジメチル2,5- ジ- (t-ブチルパー オキシ) ヘキシシ	t-ブチルパーオ キシネオデカノ エート	2,3-ジメチル- 2,3-ジフェニル ブタン
Th1 (°C)	—	122	122	141	64	259
ϵ	—	49	49	30	4	0
添加量 (質量部)	—	0.2	0.4	1.5	0.4	0.4
D2/D1	1.02	1.25	1.51	2.02	0.98	1.01
歪み硬化度	2.6	6.9	11.8	15.8	2.4	2.6
ネックイン率 (%)	18	8	5	3	20	18
発泡セル径 (μm)	180 破泡多し	95 均一	70 均一	52 均一	190 破泡多し	180 破泡多し
総合評価	×	○	○	○	×	×

[0054] (Example 4 of a comparison) As organic peroxide, except carrying out 5.5 section addition of the t-butyl peroxybenzoate (1= 122 degrees C of Th, epsilon= 49), it is the same approach as an example 1, and pelletizing was tried. However, the denaturation of the resin by organic peroxide progressed too much, the extrusion melting object became gel, and since the stable strand was not obtained, it was not able to pelletize. It was D2/D1= 3.6 of a strand.

[0055] (Example 5 of a comparison) Lacty 5000 by Shimadzu Corp., and the Easter biotechnology by the Eastman chemical company whose Tg is -30 degree C -- 8/2 -- dryblend -- carrying out -- 25mmphi -- the mouthpiece and 45mmphi single screw extruder made from Clowes MAFFAI equipped with the DISK type former made from Batten were presented, and outer-diameter 25mmphi and a pipe with a thickness of 4mm were extruded by the extrusion resin temperature of 190 degrees C, and screw-speed 70rpm. a mouthpiece -- although taken over only by making a tube support with an orthosis, without carrying out water cooling at an outlet, melting tension was insufficient and the pipe appearance was distorted by the self-weight. Charpy impact strength was 3.5 KJ/m2.

[0056] (Example 5) As organic peroxide, except carrying out 0.5 mass sections addition of the 2,2-Di-t-butyl-peroxy-butane (1= 116 degrees C of Th, epsilon= 24), when the pipe was extruded, melting tension was high, and it was round good [it was the same approach as the example 4 of a comparison, and], without a pipe appearance deforming. Moreover, Charpy impact strength is 4.2 KJ/m2, and improved compared with the time of not putting in organic peroxide.

[0057]

[Effect of the Invention] As mentioned above, as explained in detail, according to this invention, the lactic-acid system resin constituent which has the workability in which lactic-acid system resin was excellent in addition to the biodegradability which it originally has, and physical properties, a peroxide denaturation lactic-acid system resin constituent, and the Plastic solid with which it consists of them can be offered.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The lactic-acid system resin constituent characterized by becoming the lactic-acid system resin 100 mass section from the organic peroxide 0.05 whose half-life temperature (Th1) is 70-200 degrees C - the 5.0 mass sections for 1 hour.

[Claim 2] The lactic-acid system resin 100 mass section and the lactic-acid system resin constituent with which 1-hour half-life temperature (Th1) is characterized by consisting of organic peroxide 0.05 70-200 degrees C and whose hydrogen drawing multiplier (epsilon) are 10-60 - the 5.0 mass sections.

[Claim 3] The lactic-acid system resin constituent with which the aliphatic series polyester or/and the aliphatic series aromatic polyester 3 - 50 mass sections, and 1-hour half-life temperature (Th1) of 0 degree C or less are characterized [lactic-acid system resin 50 - 97 mass sections, and glass transition temperature (Tg)] by consisting of the organic peroxide 0.05 - the 5.0 mass sections which are 10-60 by 70-200 degrees C and the hydrogen drawing multiplier epsilon.

[Claim 4] The peroxide denaturation lactic-acid system resin constituent characterized by being $D2/D1=1.10-3.0$ when a lactic-acid system resin constituent according to claim 1 or 2 is made to react with a predetermined means, polydispersed degree of the lactic-acid system resin before a peroxide reaction is set to D1 and polydispersed degree of the lactic-acid system resin after a peroxide reaction is set to D2.

[Claim 5] The Plastic solid characterized by having fabricated the peroxide denaturation lactic-acid system resin constituent according to claim 4, and being formed.

[Claim 6] The Plastic solid characterized by having carried out the fabricating operation and being formed after making a lactic-acid system resin constituent according to claim 3 react with a predetermined means.

[Translation done.]